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SOLID WASTE PROGRAM

CONVERSION OF URBAN REFUSE TO OIL



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by

Herbert R. Appell, Irving Wender,
and Ronald D. Miller

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CONVERSION OF URBAN REFUSE TO OIL

by

Herbert R. Appell,¹ Irving Wender,² and Ronald D. Miller³

ABSTRACT

Urban refuse, cellulosic wastes, and sewage sludge have been converted to heavy oil by heating under pressure with carbon monoxide and steam. Conversions of the organic matter to oil, water, and gas have averaged near 90 percent at temperatures of 250° to 400° C and pressures of 1,500 to 5,000 psi. The yield of oil, based on the dry organic matter of the waste materials, is usually near 40 percent. This is the equivalent of more than 2 barrels of oil per ton of dry, ash-free waste material. The oil from urban refuse and cellulosic wastes has a sulfur content near 0.1 percent. This low sulfur content makes the oil from refuse a desirable source of fuel oil.

INTRODUCTION

The amount of solid wastes generated each year is increasing rapidly because of the increasing affluence of our society and the increased wastes due to population growth. Because of the shortage of landfill areas, this time-honored method of refuse disposal is no longer adequate and new approaches must be found. Our natural resources are not unlimited and waste disposal should be redirected to waste reclamation and reuse. The Bureau of Mines research currently in progress on the conversion of urban refuse to oil has the objective of obtaining a crude oil substitute from the organic waste materials which would normally go to landfill or be incinerated.

EXPERIMENTAL PROCEDURES

The experimental work was conducted in a 500-ml autoclave heated in a furnace fitted with a rocking mechanism. Two versions of the oil-forming process were studied. The first work was conducted at 380° C and 5,000 psig. These are the conditions under which lignite and carbohydrates had been liquefied in

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the laboratory.⁴ At these conditions it was not necessary to add water to the refuse unless its water content was less than 30 percent. The moist refuse was charged to the autoclave with 1,500 psig of carbon monoxide, and the autoclave was then heated to 380° C and held at that temperature for 20 minutes. After the autoclave had cooled it was opened, and the water was separated from the oil and residue by decantation. The oily residue was extracted with benzene to recover the oil. The benzene was then distilled off to isolate the product oil.

Experimental work was also conducted at 250° C and 1,500 psig. At these conditions 200 ml of water was added in order to maintain an aqueous phase. Although some refuse contains enough naturally occurring catalysts for oil formation to proceed, most of the laboratory work involved the addition of several percent of sodium carbonate or bicarbonate. Usually 500 psig of carbon monoxide was charged to the autoclave at 250° C. Other pressures were, however, investigated as part of the research program. The operating pressure rose to near 1,500 psig because of the steam pressure developed, the carbon dioxide liberated, and the effect of the heat in increasing the pressure of the carbon monoxide charged to the reactor. The oil obtained at 250° C was extracted with acetone, and then the acetone was removed by distillation. The oil obtained in the low-temperature version of the process contained more oxygen than the high-temperature oil, and an oxygen-containing solvent, such as a low-boiling ketone, is a better solvent than a hydrocarbon such as benzene which was used for extraction of the oil formed at 380° C.

EXPERIMENTAL RESULTS

The application of heat to crude cellulosic materials results in the loss of water accompanied by the formation of gas, small quantities of organic liquids, and a charred residue. Research on the chemistry of lignite liquefaction at the Bureau's Pittsburgh Energy Research Center has shown that the usual course of the cellulose decomposition reaction can be modified so that an oil instead of a char is obtained as a major product.

The effectiveness of carbon monoxide and steam in directing the conversion of cellulose to a benzene-soluble oil at 350° C or above is shown in table 1. The results obtained with hydrogen, which has only a small beneficial effect, are listed as a basis for comparison. In addition to the much higher yield of oil obtained in the presence of carbon monoxide, it is noteworthy that the oxygen contents of the products obtained with carbon monoxide are significantly lower than those of the corresponding products obtained with hydrogen.

The oil-forming reaction was applied to urban refuse free of metal and siliceous materials because cellulose is the largest remaining component. Other carbohydrates and fatty materials occurring in refuse are also readily converted to oil. Plastics have not yet been studied in detail but preliminary

⁴Appell, H. R., I. Wender, and R. D. Miller. Solubilization of Low Rank Coal With Carbon Monoxide and Water. Chem. and Ind. (London), No. 47, Nov. 22, 1969, p. 1703.

tests have indicated that, although some depolymerization occurs, a substantial portion of the plastic materials remains as part of the unconverted residue. Usually the plastic content of municipal refuse is only a few percent and the presence of these materials is not expected to have more than a very minor influence on oil yield or composition. The unconverted plastics can, however, be expected to increase the fuel value of the residue.

TABLE 1. - Composition of benzene-soluble oils and residues from cellulose
(2 hr at 350° C, 1,500 psig initial pressure)

Gas.....	Benzene-soluble oil		Residue	
	CO + H ₂ O	H ₂	CO + H ₂ O	H ₂
Weight percent of charge.....	40.0	5.0	10	40
Carbon.....percent..	83.3	76.3	71.4	74.9
Hydrogen.....do.....	7.8	8.2	5.9	4.6
Oxygen.....do.....	8.9	15.5	12.7	20.5
H/C.....	1.11	1.27	0.98	0.73

The experiments on refuse at 380° C and 1,500 psig initial pressure gave conversions near those previously obtained in liquefying lignite and pure carbohydrates. The yields and product distributions obtained with carbon monoxide and with hydrogen are shown in table 2. The water-gas shift reaction, wherein water and carbon monoxide react to form hydrogen and carbon dioxide, takes place readily at temperatures above 380° C. The water and carbon dioxide formed from the decomposition of the refuse in table 2 are given within limits because of the uncertainty of the exact contribution of the refuse and the water-gas shift reaction towards the final yield of the water and carbon dioxide. It appears certain, however, that in the presence of carbon monoxide, the extent of the dehydration reaction is decreased and the extent of the decarboxylation reaction is increased, both relative to the reactions occurring in the presence of hydrogen. The results of the decreased dehydration and increased decarboxylation are an increase in the hydrogen to carbon ratio and a change in the physical form of the product from a solid to a liquid.

TABLE 2. - Conversion of municipal refuse to oil
(20 min at 380° C, 1,500 psig initial pressure)

	Gas	
	CO	H ₂
Conversion.....percent..	94	80
Product distribution, weight-percent:		
Oil.....	41	18
Residue ¹	6	20
Water.....	27-36	45
CO ₂	15-24	15
Other.....	2	2

¹Composition: C, 79.6 percent; H, 9.5 percent;
N, 1.9 percent; S, 0.13 percent.

The two largest cost items in the conversion of refuse to oil are the capital investment in high-pressure equipment and the cost of carbon monoxide. After the feasibility of the conversion of refuse to oil was established, the research was directed towards determining the lowest temperatures and pressures at which the conversion would take place. This program was expected to lead to lower capital costs and carbon monoxide consumption.

An investigation of the effect of reaction time, carbon monoxide pressure, water concentration, and catalysts led to a laboratory procedure which could be conducted at relatively mild conditions. In order for oil to be formed at mild conditions (250° C, 500 psig initial carbon monoxide pressure, 1,500 psig operating pressure), sufficient water to maintain a liquid phase must be present. Catalytic agents must also be present, although some waste products, such as sewage sludge and some refuse, contain enough catalytic materials for oil formation to proceed. If low-mineral-content cellulosic materials, such as waste paper, are to be converted to oil, the aqueous solution charged to the reactor should contain 3 to 5 percent sodium bicarbonate or its molar equivalent in soluble carbonates or bicarbonates of the alkali metal or alkaline earth groups.

A major advantage of operating at temperatures near 250° C is that little, if any, of the carbon monoxide is consumed in the reaction. The mechanism by which carbon monoxide directs the conversion of cellulose and other carbohydrates to oil has not yet been resolved. It may possibly be an inhibitor of condensation reactions which lead to crosslinking of cellulose fragments. At 380° C the water-gas shift reaction occurs, and some of the hydrogen formed adds to the product. The hydrogenation of reactive intermediates is one mode of action of the carbon monoxide in liquefying cellulose, but this mechanism is largely limited to reactions occurring above 350° C.

The results of processing three different types of organic waste materials at mild conditions are given in table 3. One characteristic of oil obtained at mild conditions is the high oxygen content. This figure varies considerably with the type of material processed. Oil from waste paper usually has an oxygen content near 20 percent, whereas oil from urban refuse has an oxygen content near 12 percent. Oil from urban refuse and sewage sludge is also characterized by a nitrogen content between 2 and 3 percent. The sulfur content of all of the cellulosic wastes tested, with the exception of sewage sludge, was close to 0.1 percent. This low sulfur content is a very desirable feature of liquid fuels.

In addition to the oil yield, a water-soluble fraction resulting from hydrolysis of the cellulose is also obtained at 250° C. This material is believed to be a precursor of the oil because it can be converted to oil by recycling the aqueous solution through the process with subsequent charges of refuse. Recycle of the aqueous portion of the product, which also contains the catalyst, raises the oil yield above 40 percent. Recycle of the water from high-water-content wastes, such as wet sewage sludge, does not appear possible because water does not have to be added to this class of wastes. It may be possible that the aqueous product stream from these wastes can be used to grow yeasts for high-protein animal feeds.

TABLE 3. - Wastes to oil conversion at mild conditions

(500-ml autoclave, 500 psig initial CO pressure,
1 hr at 250° C)

	News- print	Pine needles and twigs	Sewage sludge
Waste material.....grams..	50	50	300
Water.....ml..	200	200	¹ None
NaHCO ₃ catalyst.....grams..	10	10	None
Conversion ² wt pct..	87	81	86
Oil yield ³ wt pct..	37	35.5	24.5
Product composition, wt pct:			
Carbon.....	71.7	72.2	77.0
Hydrogen.....	7.3	8.7	10.7
Nitrogen.....	(⁴)	1.05	2.80
Sulfur.....	(⁵)	0.10	0.64
Oxygen (by difference)...	-	18.0	8.8

¹The sludge was 87 percent water.

²100 less the percent unreacted.

³Based on the dry, organic matter charged.

⁴Not determined. Usually less than 0.3 percent.

⁵Not determined. Usually less than 0.1 percent.

The oil obtained from organic wastes is a dark viscous material. The oil obtained at 380° C flows slowly, but the material obtained at 250° C is a soft solid and must be warmed to impart fluidity. Infrared and mass spectrometric analysis indicate the oils to be paraffinic and cycloparaffinic with the presence of carbonyl and carboxyl groups. The high-temperature product has a very small amount of aromatic material, probably phenolic, but the low-temperature material does not appear to have any aromatic compounds.

This process is still in the laboratory stage and it is not certain that the optimum process conditions have been found. Additional research on ways to reduce the oxygen content, make the product more fluid, upgrade the crude product to useful fuels, and determine the characteristics and composition of the oil is necessary. Work on a larger scale in a continuous unit will be started soon; this will enable us to obtain cost estimates and to more thoroughly evaluate the process.

SUMMARY AND CONCLUSIONS

Cellulosic wastes, including materials such as urban refuse, wood industry wastes, and sewage sludge, have been converted to a heavy oil by heating in the presence of carbon monoxide and steam under pressure.

A high-temperature version, conducted at 380° C, and a low-temperature version, conducted at 250° C, have been developed on a laboratory scale.

The oil from cellulosic wastes, exclusive of sewage sludge, is characterized by a high oxygen content and a low sulfur content.

Additional studies in the laboratory and on a pilot plant scale are underway for cost estimates and a thorough evaluation of the process.

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